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Thermodynamics of a classical ideal gas at arbitrary temperatures

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Abstract

We propose a fundamental relation for a classical ideal gas that is valid at all temperatures with remarkable accuracy. All thermodynamical properties of classical ideal gases can be deduced from this relation at arbitrary temperature.

The famous equation of state for an ideal classical gas is

$$PV = Nk_BT\,. \tag{1}$$

Interestingly, a classical gas obeys this relation at all temperatures as long as it is ideal, i.e., the Hamiltonian of the system does not depend on the co-ordinates of the particles at all. The proof is simple, and appears in most textbooks [1]. We will also provide the proof later.

An equation of state, however, does not specify a system completely [2]. For example, from the equation of state in Eq. (1), we cannot find the entropy of the system, and many other properties for that matter. Of course if we have a fundamental relation for the system, it contains all thermodynamic information about the system including the equations of state themselves [2]. These are, for example, relations of the type $S = S(U, V, N)$ or $U = U(S, V, N)$, which express the entropy or the internal energy as a function of other extensive parameters of the system. Legendre transforms of these equations work just as well, like the Helmholtz free energy A as a function of T, V and N. However, it is often difficult to obtain such relations in closed forms which would be valid for any temperature. The Sackur-Tetrode relation, for example, is a fundamental relation of the form $S = S(U, V, N)$, but unlike the relation in Eq. (1), it is valid only if the gas is non-relativistic, i.e., if the temperature is small in the sense that $\beta mc^2 \gg 1$, where m is the mass of the gas particles. Our aim in this article is to suggest a fundamental relation for the classical ideal gas that can be used at any temperature.

Since the gas is assumed to be ideal, the energy of any particle in the gas depends only on its momentum. At a momentum p, let us denote the energy of a particle by $\varepsilon(p)$. The

single-particle partition function in the canonical ensemble is then given by

$$Q = \frac{gV}{(2\pi\hbar)^3} \int d^3p \; e^{-\beta\varepsilon(p)} \equiv \frac{g}{2\pi^2 \lambda\!\!\!^{-3}} \; V f(\beta) \,, \tag{2}$$

where g denotes the degeneracy due to internal degrees of freedom, $\lambda\!\!\!^{-}$ is the Compton wavelength of the particle divided by 2π,

$$\lambda\!\!\!^{-} = \frac{\hbar}{mc} \,, \tag{3}$$

and $f(\beta)$ is a dimensionless integral defined by

$$f(\beta) = \frac{1}{(mc)^3} \int_0^\infty dp \; p^2 e^{-\beta\varepsilon(p)} \,. \tag{4}$$

The canonical partition function for a system of N particles is then given by

$$Z = \frac{Q^N}{N!} \,, \tag{5}$$

with the Gibbs correction factor for identical particles. This gives

$$\ln Z = N \left[\ln V + \ln f - \ln N + 1 + \ln(g/2\pi^2 \lambda\!\!\!^{-3}) \right] \,, \tag{6}$$

where we have used Stirling's formula for $\ln N!$. It is to be noted that $f(\beta)$ is the only component which is not exactly known at this point. Our aim would be to determine it.

For this, we start by evaluating some thermodynamic quantities. The pressure of the gas is given by

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{\beta,N} = \frac{N}{\beta V} \,, \tag{7}$$

irrespective of the functional form of $f(\beta)$. This is Eq. (1), and this is why it is valid for any temperature.

Next we look at the energy density. This is given by

$$\varrho = -\frac{1}{V} \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V,N} = -\frac{N}{V} \frac{d \ln f}{d\beta} \,. \tag{8}$$

Thus, if we define a quantity w by

$$P = w\varrho \,, \tag{9}$$

Eqs. (7) and (8) show that

$$\frac{1}{w} = -\beta \frac{d \ln f}{d\beta} = -\frac{d \ln f}{d \ln \beta} \,. \tag{10}$$

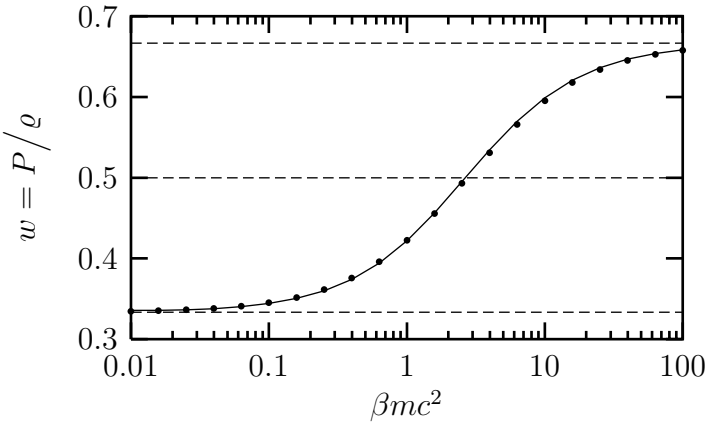

Figure 1: The ratio P/ϱ for different temperatures. The solid line is obtained by numerical integrations from Eq. (13), and the points correspond to the fit of Eq. (16). The dashed horizontal lines are drawn at $\frac{1}{3}$, $\frac{1}{2}$ and $\frac{2}{3}$.

Using the definition of $f(\beta)$ from Eq. (4), we can then write

$$w = \frac{\int_0^\infty dp\; p^2 e^{-\beta\varepsilon(p)}}{\int_0^\infty dp\; p^2 \beta\varepsilon(p) e^{-\beta\varepsilon(p)}}\,. \tag{11}$$

It is easy to see that if $\varepsilon(p) \propto p^\lambda$, this formula gives $w = \lambda/3$, which gives the correct results for the very low and very high temperature limits [1].

For arbitrary temperatures, we should use the relativistically correct formula for $\varepsilon(p)$. For an ideal gas, there is no potential energy. The kinetic energy of a particle with momentum p is given by

$$\varepsilon(p) = \sqrt{m^2c^4 + p^2c^2} - mc^2\,. \tag{12}$$

Putting this into Eq. (11) and making a change of variable, we can write

$$w = \frac{\displaystyle\int_0^\infty dy\; y^2 \exp\Big(-\xi\sqrt{1+y^2}\Big)}{\displaystyle\xi\int_0^\infty dy\; y^2\Big(\sqrt{1+y^2}-1\Big)\exp\Big(-\xi\sqrt{1+y^2}\Big)}\,, \tag{13}$$

where ξ is a dimensionless variable for the inverse temperature:

$$\xi = \beta mc^2\,. \tag{14}$$

The integrations can be performed numerically for any value of ξ. The results are shown by the solid line in Fig. 1.

The shape of the curve is very similar to a hyperbolic tangent curve. We can try a fit of the form

$$w = \frac{1}{2} + \frac{1}{6}\tanh\Big(\alpha\ln(\xi/b)\Big)\,, \tag{15}$$

with two parameters α and b which are both positive. This has the correct behavior for both extremes: $w = 1/3$ for very high temperatures ($\log\xi \to -\infty$) and $w = 2/3$ for very low temperatures ($\log\xi \to +\infty$). For reasons described below, we must take $\alpha = \frac{1}{2}$, which means that our fit is of the form

$$w = \frac{1}{2} + \frac{1}{6}\,\frac{\xi - b}{\xi + b}\,. \tag{16}$$

The choice for the parameter b will be made later, in Eq. (29). However, in order to give a preview of the goodness of this fit, we anticipate the value and show the resulting fit as points in Fig. 1. As the figure suggests, the fit is very good for all temperatures. In fact, the agreement between the fit and direct numerical calculation is considerably better than 1% everywhere.

It has to be remarked that $\varepsilon(p)$, and consequently ϱ, do not include the contribution from the rest mass energy of the particles. However, it is trivial to obtain a relation between P and the energy density ρ which includes the mass energy as well. Obviously,

$$\rho = \varrho + mc^2 n\,, \tag{17}$$

where $n = N/V$ is the number density of particles. Using Eq. (1), we can write it as

$$\rho = \varrho + \xi P \tag{18}$$

for a classical ideal gas. If we then define an equation of state in the form

$$P = \omega\rho\,, \tag{19}$$

the constant ω will have a very simple relation with w which can be obtained by dividing both sides of Eq. (18) by P:

$$\frac{1}{\omega} = \frac{1}{w} + \xi\,. \tag{20}$$

We now go back to the fit of Eq. (16), and notice that from Eq. (10), we can now determine $\ln f$. In fact, using the fit, we can write

$$\frac{d\ln f}{d\ln\xi} = -3\,\frac{\xi + b}{2\xi + b}\,, \tag{21}$$

noting that $d\ln\beta = d\ln\xi$, since mc^2 is constant. Thus,

$$\begin{aligned} \ln f &= -3\int \frac{d\xi}{\xi}\,\frac{\xi + b}{2\xi + b} \\ &= K - 3\ln\xi + \frac{3}{2}\ln(2\xi + b)\,, \end{aligned} \tag{22}$$

where K is an integration constant.

To determine this constant, we may use of the form for $\ln f$ for large ξ. In this case, small momentum values dominate the integrand, so that we can approximate $\varepsilon(p)$ by $p^2/2m$. Once this is done, the integration in Eq. (4) can be exactly performed and one obtains

$$f(\xi \gg 1) \approx \sqrt{\frac{\pi}{2}}\,\xi^{-3/2}\,. \tag{23}$$

On the other hand, for $\xi \gg 1$, Eq. (22) gives

$$\ln f(\xi \gg 1) \approx K - \frac{3}{2}\ln\xi + \frac{3}{2}\ln 2\,. \tag{24}$$

Notice that this has the correct ξ-dependece as the non-relativistic formula of Eq. (23). This is the reason why we had to take $\alpha = \frac{1}{2}$ in Eq. (15). Moreover, this also allows us to determine K, viz.,

$$K = \frac{1}{2}\ln\pi - 2\ln 2\,. \tag{25}$$

Putting this value of K into Eq. (22), we obtain

$$\ln f \;\; = \;\; \frac{1}{2}\ln\pi - 2\ln 2 - 3\ln\xi + \frac{3}{2}\ln(2\xi + b)\,. \tag{26}$$

The remaining constant b can be determined by using the asymptotic value of f for small ξ. In this case, large momentum values dominate the integrand so that we can put $\varepsilon(p) = cp$. Once this approximation is made, the integration in Eq. (4) can be performed analytically and we obtain

$$f(\xi \ll 1) \approx 2\xi^{-3}\,. \tag{27}$$

On the other hand, Eq. (26) gives

$$\ln f(\xi \ll 1) \approx \frac{1}{2}\ln\pi - 2\ln 2 - 3\ln\xi + \frac{3}{2}\ln b\,. \tag{28}$$

Comparing the two expressions, we obtain

$$b = \frac{4}{\sqrt[3]{\pi}}\,. \tag{29}$$

This finally completes the fit that we sought for. The fit is shown in Fig. 2, along with the values obtained by direct numerical integration.

It may be useful to make a comment about our choice of the parameter b. We have chosen it so as to fit the low-ξ end perfectly. However, the resulting fit is worst (though still better than 1%) for intermediate values of ξ, which shows clearly in Fig. 1. If we take a slightly smaller value of ξ, the middle part fits much better. Of course it also means that the agreement for small ξ gets a bit worse. To be precise, if instead of the value b given in Eq. (29) we choose some other value b' for the parameter under consideration, the values of $\ln f$ mismatches by an amount $\frac{3}{2}\ln(b/b')$ for $\xi \ll 1$. But since the value of $f(\beta)$ itself is very large for small values of ξ, the fractional error is very small. A choice like $b = e$, the base of natural logarithms, makes the overall fit much better, to better than 0.5%, for the entire range of temperatures. If we go further down, say $b = 8/3$, the fit becomes very good in the middle but considerably worse at the ends.

We can put our fit for $f(\xi)$ into Eq. (6). This gives

$$\ln Z = N\left[\ln\left(\frac{gV}{N\lambda\!\!\!^{-3}}\right) + \frac{3}{2}\ln\left(\frac{2\xi + b}{4\pi\xi^2}\right) + 1\right]\,, \tag{30}$$

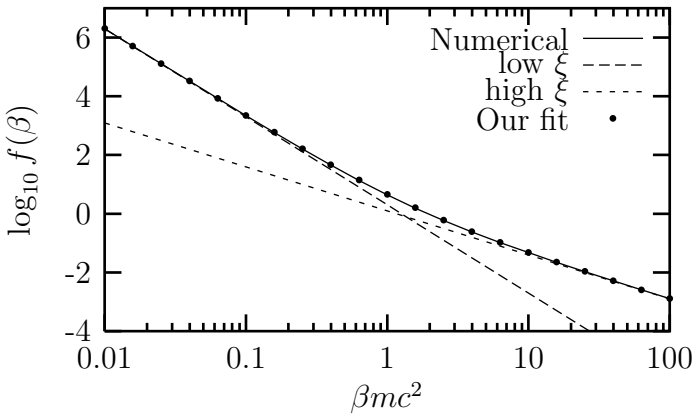

Figure 2: The integral $f(\beta)$ defined in Eq. (4), plotted as a function of $\xi = \beta mc^2$. The two dashed lines correspond to the asymptotic forms for $f(\beta)$ given in Eqs. (23) and (27).

where b is given in Eq. (29). The Helmholtz free energy of the classical ideal gas is then given by

$$A = -\frac{N}{\beta}\left[\ln\left(\frac{gV}{N\lambda^3}\right) + \frac{3}{2}\ln\left(\frac{2\xi + b}{4\pi\xi^2}\right) + 1\right]. \tag{31}$$

If we recall the definition of ξ from Eq. (14), we realize that this is an expression for the free energy as a function of the volume, temperature and total number of particles. This is thus a fundamental relation which can be used at any temperature. All thermodynamic properties of an ideal gas can then be deduced from this relation at arbitrary temperature.

This is the result. Of course it is not exact; it is a fit to the numerical results. But it is a very good fit, and the usefulness of such an expression cannot be overemphasized. In most practical situations, a closed analytic expression is much easier to use than numerical integrations. Our expression for the Helmholtz free energy in Eq. (31) provides such an analytic expression which can be used at any temperature to obtain thermodynamic properties of a classical ideal gas.

References

[1] Some of my favorite textbooks are:

a) F. Reif: *Fundamentals of statistical and thermal physics*, McGraw-Hill, 1965;

b) E. M. Lifshitz and L. P. Pitaevskii: *Statistical physics*, Part 1, Pergamon Press, 3rd edition, 1980;

c) R. K. Pathria: *Statistical mechanics*, Pergamon Press, 1972.

[2] H. B. Callen, *Thermodynamics*, John Wiley and sons, 1960. Not all thermodynamics textbooks emphasize these issues clearly.